

THE CATALYTIC ACTIVITY OF METALIZED SILICA
GELS. I HYDROGENATION REACTIONS

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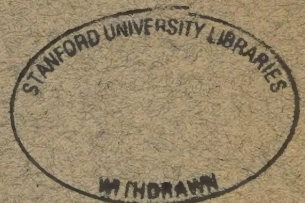
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THE CATALYTIC ACTIVITY OF METALLIZED SILICA GELS

I. THE HYDROGENATION OF ETHYLENE*

BY VLON N. MORRIS AND L. H. REYERSON

As a result of the preliminary work on the catalytic activity of metallized silica gels, reported by Reyerson and Thomas¹ it was felt that a thorough study of some simple gas reactions would throw further light upon the behavior of these active catalysts. It was decided to first investigate in a quantitative manner the reaction between hydrogen and ethylene. Pease² lists several advantages in the use of this particular reaction. In addition to the reasons advanced by Pease for using this reaction it was felt that a comparison could be made between the usual catalysts and these metallized silica gels.

In carrying out this investigation it was decided to use the streaming method because it would then be possible to analyze the products accurately. In the case of many of the static methods reported in the literature the hydrogenation of ethylene is followed manometrically. While it is highly probable that the hydrogenation takes place no proof is often given that such is the case. A study of the effect of variation of the rate of streaming and the effect of continued use on the efficiency of the catalyst made this method desirable. Silica gels metallized with platinum, palladium, and copper were used in this investigation. Preliminary experiments with silverized gel showed that it had no catalytic effect on this reaction so no further work with the silver catalyst was undertaken. Variations in temperature, in the rate of flow of the gases thru the catalyst, and in the composition of the gas mixture were studied more or less independently of one another.

Experimental

The silica gel used in the preparation of these catalysts was prepared essentially as described by Patrick³. This silica gel was metallized by the method of Latshaw and Reyerson⁴ except in the case of a part of the copper catalyst. Thorough outgassing of the silica gel was found to be essential before the hydrogen was admitted to the gel. Failure to do this resulted in diminished adsorption of hydrogen and a corresponding lack of reduction of metal ions to the metal. In the preparation of the platinized and palladized gels solutions of platinous and palladious salts were used. The solution containing the platinous ions was prepared by reducing a solution of chloro-

* The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by V. N. Morris (Du Pont Fellow in Chemistry 1925-26) in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1926.

¹ "Colloid Symposium Monograph," 3, 99.

² J. Am. Chem. Soc., 45, 1196 (1923).

³ U. S. Patent, 1297724.

⁴ J. Am. Chem. Soc., 47, 610 (1925).

platinic acid by means of sulphur dioxide while the solution was hot. It was found that it was impossible to remove all of the sulphur dioxide from the solution and thereby prevent its appearance in the final product. The solution containing the palladious ions was prepared by dissolving ammonium chloropalladite.

In the case of the copperized gel one of the samples of catalyst was prepared as already indicated using a solution of cupric chloride. The reduction of the cupric ion is always incomplete under these conditions so that the product was dried and the reduction completed above 200° by hydrogen. The other samples of the copper catalyst were prepared by just covering the silica gel with N/5 copper nitrate solution and drying in an atmosphere of hydrogen and then completing the reduction with hydrogen above 250° . It was noticed rather early in the work that samples of the catalysts left exposed to laboratory air tended to change color. The platinized and palladized gels tended to change from black to gray black and then gray while the copperized gels usually became greenish in color. These changes were attributed to oxidation due to laboratory fumes. The catalysts were therefore kept in tightly stoppered bottles and no appreciable changes were noted under these conditions.

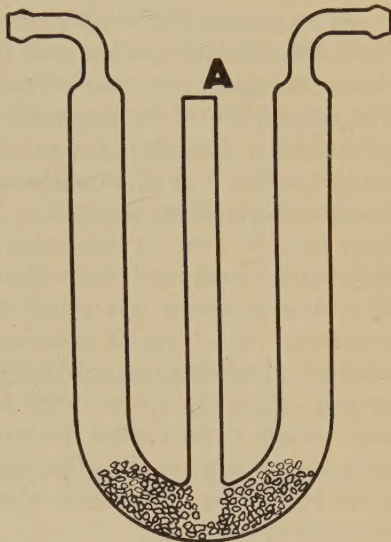


FIG. 1

In carrying out the catalytic hydrogenation the hydrogen and ethylene were first collected in the desired proportions in a four liter bottle by displacing water from the full bottle until water remained to a depth of about five centimeters. The water was forced from the bottle through a tube, into a reservoir above, by the pressure of the gases being introduced. The bottle was then thoroughly shaken to mix the gases and also to saturate the water. The gases were then forced through a drying tube and into the tube carrying the catalyst by means of water flowing from the reservoir above the bottle. A screw clamp on the tube connecting the reservoir with the bottle made it possible to regulate the flow of water and thereby control the volume of gas streaming through the catalyst per unit time.

The hydrogen used in these experiments was commercial electrolytic hydrogen and analyses showed it to be practically pure hydrogen. The ethylene used was obtained from the Ohio Chemical Company of Cleveland, Ohio. This gas analysed about ninety-eight percent ethylene. No attempt was made to remove the residual impurities except to bubble the gas through distilled water before collection in the four liter bottle.

From the bottle the mixed gas was passed through a calcium chloride drying tube and then through the tube containing the catalyst. The catalyst tube was made of Pyrex as shown in Fig. 1. The bottom of the tube was always filled with sufficient catalyst so that the gas mixture had to pass through the catalyst. The same amount of catalyst i. e. 3.5 grams was, used in each case. The shape of the catalyst tube made it possible to immerse the lower part of the tube in the various constant temperature baths used. A thermometer was inserted through tube A and the bulb of the thermometer was kept immersed in the catalyst. The thermometer was held in tube A by a section of rubber tubing. This sealed the top of the tube and prevented the escape of gases through this tube.

After passing the catalyst the gases were allowed to escape into the air for a few minutes until it was felt that the system had reached a steady state. The gases were then collected in a gas burette for purposes of analysis. The rate of flow of the gases was determined by the rate of collection in the gas burette. The reaction was followed by the determination of the ethylene content before and after reaction. These determinations were made by the usual methods of gas analysis. The disappearance of ethylene was checked from time to time by analysing for ethane formed. The results of these determinations showed that within the limits of experimental error the amount of ethane produced was equal to the amount of ethylene which had disappeared. As a typical experiment it was calculated from the amount of ethylene which disappeared that there should be 5.43 cc. of ethane in the gas sample. Actually 5.5 cc. were found. The agreement was thought to be close enough to prove that the product of hydrogenation was ethane. Blanks were always run on the gases used before each set of experiments and any slight corrections found were always included in the actual analysis of the products of reaction.

In carrying out the experiments a study of three variables was made. For the study of the effect of variation of the temperature a constant flow of gas through the catalyst was maintained at 60 cc. per minute. The catalyst tube was maintained at constant temperature throughout each run by immersing the tube in a constant temperature bath. Experiments were run at 0°, 30°, 60°, 90°, 150°, and 240°. The gas mixtures used in these determinations were those having twenty-five per cent or less of ethylene. For the experiments on the effect of variation of the rate of flow a temperature of 60° was chosen for the platinum and palladium catalysts and 240° for the copperized gel. This was done because copper had been found, during the first experiments, to be the most efficient at that temperature while the efficiency of the other two catalysts was as high at 60° as at any other temperature. Copperized gel prepared by the second method was used in the above experiments. Gas mixtures containing 33 per cent ethylene were used in this series of experiments with the hope that the efficiency of the catalysts might be diminished sufficiently to make noticeable the effects produced by changes of rate of streaming through the catalyst. The study of the effect of the variation of the composition of the gas mixtures was made at two tempera-

tures i.e. 27° and 170°. Copperized gel prepared by the first method was used in this set of experiments. The composition of the mixture varied from about 12 per cent ethylene to more than 80% ethylene and the rate of flow was maintained at 100 cc. per minute. The tables give the actual percentages as determined by analysis in all cases.

Results

In determining the efficiency of the catalyst it has often been customary to neglect volume changes in the calculations. The efficiency of these catalysts was so great however, that large volume changes occurred and it was therefore necessary to take this into account in the calculations. The easiest method of handling this was to base the expressions on the percentages of ethylene present before and after reaction. Let a be the number of moles of ethylene in a given volume of the gas mixture before reaction and b the corresponding number of moles of hydrogen. If x is the fraction of ethylene hydrogenated then the number of moles of ethane, ethylene and hydrogen in the mixture after reaction will be ax , $a-ax$ and $b-x$ respectively. If P_1 is the percentage of ethylene in the original mixture, and P_2 the percentage in the final mixture, it follows that

$$\frac{P_1}{100} = \frac{a}{a+b} \quad (1)$$

$$\frac{P_2}{100} = \frac{a-ax}{a-ax+ax+b-ax} = \frac{a-ax}{a+b-ax} = \frac{1-x}{\frac{a+b}{a}-x} \quad (2)$$

As a result of substituting the value of equation (1) in equation (2) we have the following:

$$\frac{P_2}{100} = \frac{1-x}{\frac{100}{P_1}-x} \quad (3)$$

From (3) the value of x comes out to be

$$x = \frac{P_1 - P_2}{P_1} - \frac{(100)}{100 - P_2}$$

This expression was used in all cases in which the ethylene constituted less than 50 percent of the gas mixture. In the cases in which the percentage of ethylene was greater than that of hydrogen the same equation was used except that the calculations were based on the percentages of hydrogen so that the terms of the equation had a different meaning.

Table I gives the results of the experiments on the effect of temperature variation on the efficiency of the catalysts. Each value given represents the average of from two to six determinations. The temperatures given are the temperatures of the catalysts at the time sampling was started. This temperature did not represent the actual temperature of the catalyst throughout the experiment as a rise of as much as 20° was noted on the thermometer

which was immersed in the catalyst itself. This was especially true at the lower temperatures. The results shown for copper represent the average of six separate determinations and the catalyst was prepared by the saturation of the gel with copper nitrate solution, followed by reduction with hydrogen. There was a variation of as much as two percent in the determinations on the copper catalyst so that six determinations were made and the results averaged.

TABLE I
The Effect of Temperature on the Hydrogenation of
Ethylene in the Presence of Metallized
Silica Gels

Temperature	Percentage of Ethylene		Percentage of hydrogenation
	Before reaction	After reaction	
Palladized Silica Gel Catalyst			
240°	23.4	1.8	94.0
150°	23.4	0.7	97.7
90°	23.4	0.2	99.3
60°	23.4	0.1	99.7
30°	23.4	0.2	99.3
0°	23.4	0.2	99.3
Platinized Silica Gel Catalyst			
240°	25.7	0.6	98.3
150°	25.7	0.5	98.5
90°	25.7	0.5	98.5
60°	25.7	0.4	98.8
30°	25.7	0.4	98.8
0°	25.7	0.4	98.8
Copperized Silica Gel Catalyst			
360°	25	15.0	47.1
240°	25	11.8	59.9
150°	25	13.1	54.7
90°	25	13.9	51.6
60°	25	18.5	32.0
30°	25	22.4	13.5
0°	25	21.2	18.3
-20°	25	19.2	28.7

Fig. 2 represents the results of these experiments graphically. The determination at -20° for the catalyst is of doubtful value because adsorption of ethylene is probably so great as to render the measurements inaccurate.

Table II gives the results of the study on the variation of the rate of streaming of the gas through the catalysts. The same catalysts were used as in the first experiments.

TABLE II
The Effect of the Rate of Streaming on the Activity
of the Catalysts

Rate of Flow per minute	Percentage of Ethylene		Percentage of hydrogenation
	Before reaction	After reaction	
Palladized Silica gel catalyst at 60°			
52.2 cc.	32.2	0.1	99.8
127.7	32.2	1.2	97.4
200	32.2	2.5	94.5
316	32.2	3.4	92.6
Platinized Silica Gel Catalyst at 60°			
57.7 cc.	32.2	1.3	97.2
103.6	32.2	3.9	92.5
171.4	32.2	7.3	83.4
273.0	32.2	9.1	78.6
600	32.2	10.4	72.1
Copperized Silica Gel Catalyst at 240°			
22.0 cc.	32.9	10.5	74.8
92.3	32.9	20.8	43.8
240.0	32.9	25.6	26.2

Fig. 3 graphically represents these results.

Table III gives the results of the study on the variation in the composition of the gaseous mixture as it affects the activity of the catalysts at 27° and 170°.

TABLE III
The Effect of the Composition of the Gaseous Mixture in the Hydrogenation
of Ethylene at 27°.

Percentage of gases before reaction		Percentage of Ethylene after reaction for each catalyst			Percentage of Hydrogenation for each catalyst		
Ethylene	Hydrogen	Palladium	Platinum	Copper	Palladium	Platinum	Copper
Temperature of 27°							
15.7		0.5	0.4	13.7	97.4	97.9	14.7
23.9		1.1	0.6	23.6	96.5	98.1	1.3
49.2	46.2	20.4	19.4	48.7	75.4	77.1	2.0
72.9	22.3	72.8	72.0	72.8	0.5	5.5	0.5
Temperature of 170°							
12.4		0.4	3.1	11.0	97.2	77.4	12.7
30.9		1.3	12.0	30.0	97.1	69.5	4.2
45.4		11.2	31.1	44.6	84.8	45.7	3.0
67.3	27.8	61.7	62.7	66.8	26.0	21.5	2.5
82.9	12.2	82.9	82.9	82.8	0.0	0.0	1.0

Figures 4 and 5 graphically represent the results of these experiments.

Discussion of results

The curves shown in Fig. 2 indicate a very normal behavior for the platinum and palladium catalysts. The slightly diminished activity at higher temperatures can no doubt be attributed to diminished adsorption. The curve for copper however is unusual. In all of the experiments minimum activity was observed in the neighborhood of 30° and maximum activity at a temperature of 240° . A possible explanation of the behavior of the copper catalyst lies in the fact that a copper hydride may be forming. Adsorption measurements of Reyerson and Swearingen¹ show that the copperized gel does adsorb

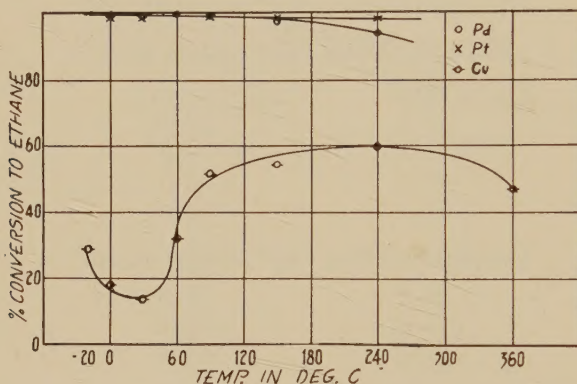


FIG. 2

The Effect of Temperature on the Catalytic Hydrogenation of Ethylene.

more hydrogen than silica gel itself at 0° . The copper of the catalyst is therefore adsorbing hydrogen. If the assumption is made that the copper is able to combine with this hydrogen under certain conditions to form a copper hydride and that this product is most stable at room temperature then we have a logical explanation of the behavior of the copper catalyst. Experiments were therefore carried out to confirm this assumption. An attempt was made to prepare the product, called copper hydride, by the usual method. This consists in mixing solutions of hypophosphorous acid and copper sulfate. An experiment was carried out at 0° and no precipitate had formed at the end of a two hour period. The mixture was then allowed to warm up to 10° for a period of six hours and still no precipitate formed. At the end of twelve hours the temperature had reached 22° and a precipitate had formed. If the solutions were mixed at room temperature a chocolate brown precipitate formed almost at once. At 100° a precipitate of a somewhat different color formed. These two precipitates were treated with concentrated hydrochloric acid. A vigorous evolution of gas occurred in the case of the precipitate formed at room temperature. The gas burned readily and gave every evidence of being hydrogen. Some metallic copper remained after treatment. The product prepared at 100° did not give enough gas to ignite when subjected to the same treatment and a larger residue of metallic copper remained. It is

¹ J. Phys. Chem., **31**, 88 (1927).

evident that the precipitate in both cases has some metallic copper in it and that a greater amount of material, capable of liberating hydrogen, is formed at room temperature than at 100°. A sample of the catalyst after being used at 30° was treated with concentrated hydrochloric acid. The metal deposit on the gel dissolved immediately with the evolution of some gas. The quantity of gas however was too small for testing. There was so little copper in the catalyst that this result was expected. However, the substance in the gel was completely dissolved as soon as the acid came in contact with it which would indicate that the copper had combined with the hydrogen.

These experiments indicate the probable formation of copper hydride in the catalyst, and that it is formed very readily at room temperature. Such formation during the process of catalysis would no doubt cut down the activity of the catalyst. As the experiments indicate at higher temperatures less hydride is formed. Furthermore any hydride that formed would be less stable as the temperature increased. Hydrogen liberated by decomposition would be likely to react as it was liberated. Thus at higher temperatures the combined effect, of catalysis due to adsorption by copper itself and the reaction resulting from the hydrogen liberated by hydride decomposition, would appear.

The experiments on the change of rate of flow indicate a fall in efficiency with increased rate of streaming through the catalysts. The fall in efficiency is not very great however for the platinum and palladium catalysts. In the case of copper the efficiency diminishes considerably as the space velocity increases. These results, as well as much of the work presented in this paper, find explanation in the idea that the most active areas in a catalyst material are those having atoms in an unsaturated or extra lattice condition.¹ The method employed in the production of the platinum and palladium catalysts must of necessity produce a great number of metal atoms, on the silica gel surface, which are not in the crystal lattice of the metal. Thus the catalysts would be expected to be very active and such is the case. X-ray analysis of these catalysts, as reported by Reyerson, Harder and Swearingen,² tends to confirm this point of view. The copper catalyst was not produced in the same way since reduction was always completed at higher temperatures whether the first reduction was by adsorbed hydrogen or not. This would reduce the number of active centers since the metal atoms nearest the gaseous conditions would distill to a less active condition. Under like conditions the efficiency of the copperized gels has always been found to be less than that of the other two catalysts. The curve shown for the copper catalyst in Fig. 3 is therefore to be expected.

The curves in Figs. 4 and 5 show conclusively that the efficiency of the catalysts is inversely proportional to the partial pressure of ethylene. The palladium and platinum catalysts show zero efficiency before the gas mixture

¹ See, for example, "Fourth Report of the Committee on Contact Catalysis." Taylor: *J. Phys. Chem.*, **30**, 145 (1926).

² *J. Phys. Chem.*, **30**, 1623 (1926).

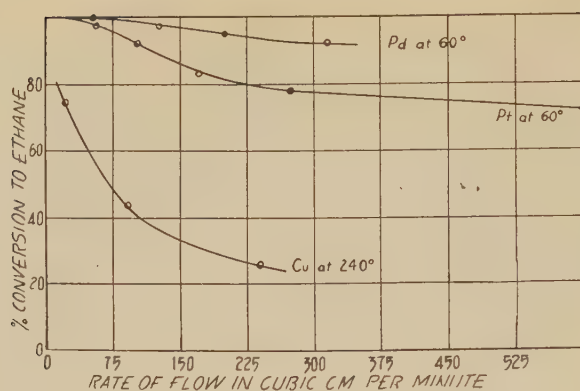


FIG. 3
The Effect of Rate of Flow of the Gaseous Mixture.

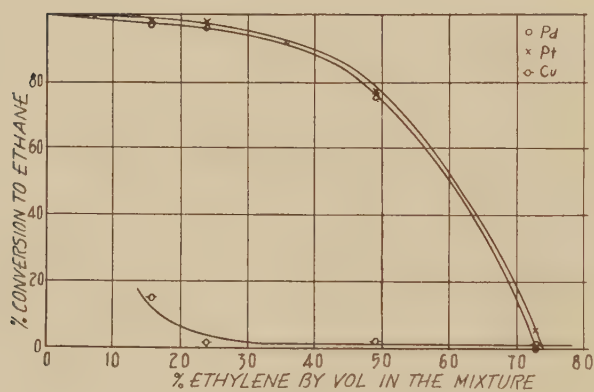


FIG. 4
The Effect of Variation in the Reaction Mixture at 27°C.

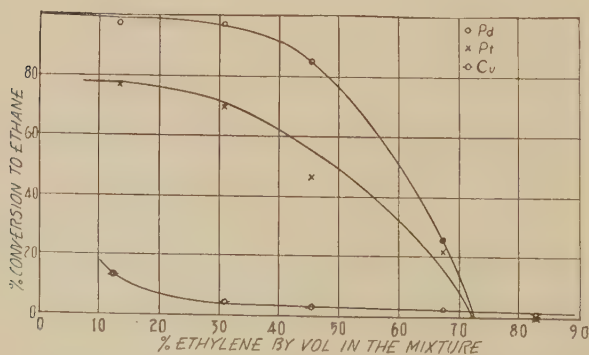


FIG. 5
The Effect of Variation in the Reaction Mixture at 170°C.

becomes eighty per cent ethylene. The logical explanation of these results is found in the proposals of Langmuir¹. The ethylene molecules which are adsorbed are oriented on the surface of the catalyst so that they will no longer react with the hydrogen molecules which strike the surface. On the other hand the hydrogen molecules which are adsorbed on the surface are capable of reacting with the ethylene molecules which strike the surface. Ethylene is much more strongly adsorbed by these catalysts than is hydrogen. Therefore, as the partial pressure of ethylene is increased, the fraction of the surface covered by ethylene molecules increases very rapidly. The active centers of the platinum and palladium catalysts thus appear to be completely covered with ethylene molecules while the partial pressure of hydrogen is still nearly one-fourth of the total gas pressure. The copper catalyst does not reach zero activity in the experiments as carried out in this investigation. This is probably due to the fact that the active copper surfaces do not hold the ethylene molecules so firmly. Another explanation for the observed results may be that suggested earlier in this paper to account for the unusual behavior of copper, that is the formation of copper hydride. A small amount of copper hydride forming and decomposing may account for the slight activity of the copper which persists after the platinum and palladium catalysts had ceased to act.

Summary

1. Platinized and palladized silica gels show marked activity as catalysts in the hydrogenation of ethylene over a considerable range of temperatures.
2. Copperized silica gel shows an unusual and variable activity in the same reaction. The possibility of hydride formation is suggested in explanation of this behavior.
3. The efficiency of these catalysts is inversely proportional to the partial pressure of the ethylene in the gaseous mixture.

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¹ Trans. Faraday Soc., **17**, 607, 621 (1921-22).

THE CATALYTIC ACTIVITY OF METALLIZED SILICA GELS II. THE HYDROGENATION OF ACETYLENE

BY V. N. MORRIS¹ AND L. H. REYERSON

The hydrogenation of acetylene was one of the projects included in von Wilde's² pioneer work on the catalytic hydrogenation of organic compounds. In 1874 he observed that acetylene will unite with hydrogen to give ethylene and then ethane in the presence of platinum black. Several years later, Sabatier and Senderens³ studied the hydrogenation of this compound in the presence of nickel and copper catalysts. Of the more recent work, that of Ross, Culbertson and Parsons⁴ is noteworthy. They found that in the presence of a nickel catalyst it was possible to obtain nearly complete conversion of acetylene to ethylene under proper conditions. That reduction to ethylene may also occur in the presence of colloidal palladium is indicated by the work of Paal and Hohenegger.⁵

The present investigation was undertaken with the primary object of obtaining information regarding the effectiveness of metallized silica gels as catalysts in connection with this reaction. These catalysts, which consist of very finely divided metals reduced at low temperatures within the pores of the adsorptive supporting material, silica gel, might be expected to exhibit properties somewhat different from those of catalysts in the more common forms. The results of x-ray examinations of and adsorption studies with metallized silica gels have recently been reported.⁶

Experimental

The methods and apparatus used in the present experiments were quite similar to those employed by the authors in connection with an earlier investigation, that of the hydrogenation of ethylene.⁷ Each catalytic sample used consisted of 3.5 grams of the metallized gel. Each catalyst was kept in a separate catalyst tube throughout the investigation. These tubes were placed side by side in the bath used to maintain temperature control, and were so connected that the gas stream could be directed through any one desired. The tendency towards fluctuations in the compositions of the original mixtures of acetylene and hydrogen was considerably lessened by making use of a saturated solution of sodium chloride as a confining liquid in the aspirating system.

¹ du Pont Fellow, University of Minnesota, 1925-26.

² Von Wilde: *Ber.*, **7**, 352 (1874).

³ Sabatier and Senderens: *Compt. rend.*, **128**, 1173 (1899); **130**, 1559 (1900).

⁴ Ross, Culbertson and Parsons: *J. Ind. Eng. Chem.* **13**, 775 (1921).

⁵ Paal and Hohenegger: *Ber.*, **48**, 275 (1915).

⁶ Reyerson and Swearingen: *J. Phys. Chem.*, **31**, 88 (1927); Reyerson, Harder and Swearingen: **30**, 1624 (1926).

⁷ Morris and Reyerson: *J. Phys. Chem.*, **31**, 1220 (1927).

The particular platinum catalyst used was reduced originally by means of adsorbed hydrogen at a temperature of about -20° . Prior to its being used in catalytic studies, it had been given an additional treatment with hydrogen at 100° . The palladium catalyst was reduced originally in similar fashion and had also been given additional treatments with hydrogen at higher temperatures.

The acetylene was prepared by the action of water on calcium carbide. The removal of the most deleterious impurities, phosphine and hydrogen sulfide, was accomplished by using the method of Berge and Reychler.¹ The gas was stored over water in a large bottle. The freshly prepared gas was absorbed by bromine to the extent of 97.6 per cent.

The electrolytic hydrogen used was passed through a purification train containing solutions of pyrogallate, permanganate and sulfuric acid. Its purity, as determined by the explosion method, was 96 per cent.

Although the determination of the acetylene and hydrogen in the original mixtures presented no difficulties, the same was not true for the analyses of the effluent gases. These latter contained not only acetylene and hydrogen, but also the reaction products, ethylene and ethane. Several methods for distinguishing between ethylene and acetylene were tried before that of Ross and Turnbull² was adopted. According to the method of these authors, acetylene may be determined in the presence of ethylene by titrating the nitric acid liberated by the reaction of the former gas with a solution of silver nitrate. This reaction is represented by the following equation:



The total unsaturated gas may be determined in another sample by absorption in bromine, and the ethylene thus obtained by difference.

Since a considerable decrease in volume accompanies the reactions, and the change in volume in one case is often much greater than in another, the tabulation of the actual percentages of the various substances in the mixtures before and after catalysis does not give a very clear indication of the extent to which reaction has taken place. Although an equation for calculating the percentage conversion was developed, there appeared to be so many possible sources of error in employing it that the results obtained by its use have not been recorded.

Results

At the time the experimental work was carried out, it was thought that decomposition and polymerizations of the acetylene took place only to a small extent. Since there appeared to be no violent heating of the catalysts, nor any evidence of the formation of liquid hydrogenations (such as were reported by Sabatier and Senderens³ when using nickel and copper catalysts) no analyses were made for any products other than ethylene and ethane. In reviewing the results of analyses, it appears to be highly probable that other products

¹ Berge and Reychler: *Bull.*, **17**, 218 (1897).

² Ross and Turnbull: *J. Am. Chem. Soc.*, **41**, 1180 (1919).

³ Sabatier and Senderens: *Compt. rend.*, **128**, 1173 (1899); **130**, 1559 (1900).

were formed in certain cases, since the volume of that gas which escaped detection in the analytical procedure followed was often increased by passage over the catalysts to a much greater extent than could be explained on the basis of the changes in volume which accompany reaction. Any liquid or solid products formed could easily have escaped detection by being held in the silica gel.

Effect of Variation of the Temperature. During the study of the effect of variation of the temperature, the rate of flow of the exit gases was approximately 60 cc. per minute. New mixtures of acetylene and hydrogen were made up each time the temperature was changed. Although the attempt to have all the mixtures of approximately the same composition was not entirely successful, the ratio of hydrogen to acetylene was always somewhat greater than that theoretically required for the formation of ethane. The experimental results are shown in Table I.

TABLE I
The Effect of Variation in Temperature on the
Hydrogenation of Acetylene.

Temp.	Catalyst.	Comp. of the original mixture		Comp. of the Final Mixture			
		C_2H_2 %	H_2 %	C_2H_2 %	H_2 %	C_2H_4 %	C_2H_6 %
0°	Pd	27.4	66.1	23.6	64.8	0.3	1.1
50	Pd	24.8	66.2	0.5	34.2	15.5	26.7
100	Pd	20.2	67.6	2.9	59.8	2.8	18.3
0°	Pt	27.4	66.1	24.0	66.3	2.7	0.4
50	Pt	24.8	66.2	21.9	61.2	1.7	1.7
100	Pt	20.2	67.6	1.6	49.1	6.1	19.7

In addition to platinum and palladium, a copper catalyst was also tried. At 100°, it exhibited little if any activity. At 200° it proved to be a fairly good catalyst for the production of ethane. None of the catalysts were effective at 0°: palladium was active at 50° and above; platinum at 100°; and copper at 200°.

Palladium and platinum tend to catalyze the formation of both ethylene and ethane in general. The production of ethylene is quite interesting, particularly in view of the fact that hydrogen more than sufficient for the formation of ethane was always present. For some reason the production of ethylene in the presence of palladium at 100° was much less than at 50°. An attempt to repeat this run latter led to rather inconclusive results, as the mixture made up was not the exact duplicate of that used in the original experiment.

Effect of Variation in the Reaction Mixture. In the investigation of the effect of variation in the composition of the reaction mixture, the temperature was maintained at 100°, and the rate of flow of the exit gases at 30 cc. per minute. The results are shown in Table II.

TABLE II
The Effect of Variation in the Reaction Mixture
on the Hydrogenation of Acetylene.

Catalyst	Comp. of Orig. Mixture		Comp. of Final Mixture			
	C ₂ H ₂ %	H ₂ %	C ₂ H ₂ %	H ₂ %	C ₂ H ₄ %	C ₂ H ₆ %
Pd	8.2	80.2	0.5	56.8	2.6	10.1
Pt	8.2	80.2	0.0	61.5	0.2	11.1
Pd	18.4	70.5	1.8	53.6	8.6	9.7
Pt	18.4	70.5	0.0	51.3	2.3	16.6
Pd	38.0	52.7	9.5	31.6	31.3	1.2
Pt	38.0	52.7	8.1	46.8	24.3	1.3
Pd	47.2	41.3	31.9	21.4	27.0	7.3
Pt	47.2	41.3	42.9	25.7	12.1	7.5
Pd	65.2	22.0	62.2	6.4	10.0	1.3
Pt	65.2	22.0	64.7	14.4	3.0	2.3

Discussion

There are certain obvious differences in the behavior of palladium and platinum as catalysts. Palladium appears to be the better catalyst for the production of ethylene, regardless of the original mixtures used. Platinum, on the other hand, is somewhat more effective from the standpoint of the production of ethane. Platinum appears to catalyze the more complete total hydrogenation of the acetylene when the hydrogen is in excess, but palladium is more effective when the acetylene is in excess.

The most interesting information contained in Table II has to do with the availability of these catalysts for the production of ethylene by the hydrogenation of acetylene. The ratios of ethylene to ethane, resulting from the catalysis of the reaction in the case of a mixture containing originally 37.9 per cent acetylene and 52.7 per cent hydrogen, compare very favorably with the best ratios of these two products obtained by Ross, Culbertson and Parsons¹ after a rather thorough study of the use of nickel as a catalyst for this reaction in a static system. On account of the greater excess of hydrogen and the larger amount of impurities in the gases used in the present work, the actual percentages of ethylene in the resulting mixtures were not as high as those obtained by these investigators. In view of the favorable results already obtained, it appears that a further investigation, having as its purpose the determination of the best conditions for the production of ethylene from acetylene in the presence of platinized and palladized gels, should yield gratifying results.

An interesting point in favor of the use of silica gel as a supporting material can be made after comparing the present procedure with that followed by

¹ Ross, Culbertson and Parsons: J. Ind. Eng. Chem., 13, 775 (1921).

Ross, Culbertson and Parsons. These investigators found that ethane was the almost exclusive product of the reaction unless the catalyst were given a very special treatment. On account of the strong tendency of nickel to adsorb hydrogen, a satisfactory yield of ethylene was only obtained after repeated treatments of the nickel catalyst with acetylene, which latter gas gradually tended to displace the adsorbed hydrogen. Even after this treatment it appears probably that the catalyst could not have maintained its activity for ethylene formation in a dynamic system.

With metallized silica gels, on the other hand, this laborious treatment of the catalysts is not necessary, ethylene being readily produced when the proper mixtures are passed over the catalysts. Although platinum and palladium adsorb hydrogen as a rule at least as strongly as does nickel, the gel itself undoubtedly has a much stronger adsorption for acetylene than for hydrogen, and as has recently been pointed out by Rideal and Taylor,¹ "it is possible that one of the functions of a support material is to provide the catalyst with a reservoir of one or more of the reactants." In view of the fine state of subdivision of the metals in metallized gels, it does not appear to be unreasonable to assume that the adsorption by the silica adjacent to active metal atoms may have an influence on the progress of the catalytic reaction. The adsorptions of acetylene by the metallized gels have not been measured.

This seems especially plausible if the assumption is made that reaction results only when an acetylene molecule comes in contact with a hydrogen molecule adsorbed by the active catalytic centers. The results of this investigation are not complete enough to support this view definitely; but the evidence points strongly in that direction. If the above assumption is made, then of course the ethylene first produced must strike another hydrogen molecule adsorbed on the surface before ethane is formed. The results given in Table II tend to confirm this assumption. From kinetic considerations it is evident that when the partial pressure of hydrogen is high as compared to acetylene then the number of acetylene molecules striking the hydrogen molecules already on the catalytic surface will be small compared to the number of hydrogen molecules reaching these same points. Reaction under the conditions of the above experiments would then be rather small. With an increase in the partial pressure of acetylene the chance of an acetylene molecule striking a hydrogen molecule already adsorbed by the catalyst would be materially increased. This would be the case even though the hydrogen molecules were as yet more successful in the competition for any uncovered areas of the catalytic surface. However, as the percentage of acetylene in the gas mixture increases the acetylene molecules will be more and more successful in reaching the uncovered areas. They will no doubt be much more strongly adsorbed so that finally the total active area of the catalyst will tend to be covered by acetylene molecules and reaction will practically cease. The results obtained in these experiments indicate that the above assumptions give a reasonable picture of the mechanism of the reaction. Additional experiments are planned in order to further confirm the above point of view.

¹ Rideal and Taylor: "Catalysis in Theory and Practice," 122 (1926).

Summary

Both ethylene and ethane are produced during the hydrogenation of acetylene in the presence of metallized silica gels. As the temperature is raised, the metals become effective catalysts in the following order: palladium, platinum, and copper. As the ratio of acetylene to hydrogen in the original mixture is increased from about 1 to 10 up to 3 to 1, the production of ethylene goes through a distinct maximum. It appears to be probable that the combined adsorptions of gel and metal produce a more satisfactory condition for the catalysis of the formation of ethylene than would the adsorption of either alone.

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VITA

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